

IN THE SPECIFICATION

THE BRIEF DESCRIPTION OF THE DRAWING, bridging pages 2 and 3, is amended to read:

BRIEF DESCRIPTION OF THE DRAWING DRAWINGS

Figure 1 is a schematic illustration of the synthetic pathway for SPPEK;

~~Figure 2 is a ^1H -NMR spectrum of PPEK in CDCl_3 , an illustration of the structural formula of PPEK;~~

~~Figure 3 is a ^1H -NMR spectrum of SPPEK in DMSO-d_6 , an illustration of the structural formula of SPPEK;~~

~~Figure 4 is a ^{13}C -NMR spectrum (hydrogen decoupled) of PPEK in CDCl_3 ;~~

~~Figure 5~~ 4 is a FT-IR spectra of PPEK and SPPEK;

~~Figure 6~~ 5 is a graph illustrating TGA traces of PPEK and SPPEKs;

~~Figure 6 is a graph of Conductivity of SPPEKs of various DS; and~~

~~Figure 7 is a graph illustrating the Conductivity of SPPEK;~~

~~Figure 8~~ 7 is a graph of Conductivity versus temperature for SPPES and SPPESK; and

~~Figure 9 is a graph of Conductivity of SPPEKs of various DS.~~

The paragraphs following the heading "NMR," at the bottom of page 7, through line 14 on page 9, are amended to read:

In order to determine the sulfonation site and the DS quantitatively, the ^1H -NMR spectra of PPEK in CDCl_3 (Figure 2) and SPPEK in DMSO-d_6 (Figure 3) were characterized. The number system adopted for the protons in the polymer and the derivatives are shown in ~~Figure 2 to 4~~ Figures 2 and 3. The careful and accurate assignments of NMR spectral signals was essential for determining both the DS and the site of sulfonation.

The starting point for peak assignment of ^1H and ^{13}C -NMR of PPEK was from the absorptions resulting from atoms surrounding the electron rich ether moiety. In a PPEK repeat unit, the hydrogen atoms at the ortho position to the ether linkage are more shielded than any other hydrogen atoms due to resonance effect of the oxygen lone pair electrons. The other functional groups present in PPEK have a deshielding effect on nearby nuclei. As a result of that, the furthest upfield signals (7.08-7.30 ppm) arise from the 4H ortho to the ether linkage. 2D COSY NMR as well as simple homonuclear decoupling experiments showed the presence of two separate spin coupling systems originating from these high field signals (Figure 2). These interactions are a result of spin-spin coupling between the hydrogen atoms at the ortho and meta positions of these phenol rings. One spin system consists of the high field ortho ether 2H absorption at 7.16-7.30 ppm coupled with the distinct signal at 7.60-7.72 ppm. The other spin system consists of the high field ortho ether 2H absorption at 7.08-7.16 ppm coupled with the multiple absorptions at 7.76-8.06 ppm.

The results of a simple ^{13}C -NMR experiment allowed formal assignment of the preceding hydrogen signals, which are key components for the accurate measurement of the DS of SPPEKs. The In the H-decoupled ^{13}C -NMR spectrum of PPEK is displayed in Figure 4. The, not shown, the carbon peaks of particular interest are the ones arising from carbon atoms directly linked to an electron-withdrawing heteroatom (N or O) causing absorptions to appear at lower field (144-195 ppm). The furthest downfield signal (193.6-194.8 ppm) is unequivocally from the ketone carbon. Further upfield, three carbon signals (155-162 ppm) arise from carbon atoms linked to electronegative oxygen atoms in the phthalazinone and ether functionalities. Finally, the less electronegative

nitrogen atoms give the carbon absorptions at higher field (144-148 ppm). In one ¹³C-NMR experiment, a spectrum was acquired with decoupling of one of the hydrogen frequencies (7.60-7.72 ppm) responsible for the 2H at the meta position of one of the phenol rings. The resulting spectrum was compared with a ¹³C-NMR spectrum acquired with full hydrogen coupling. Of all the downfield carbon signals, the C-O absorption at 156.0-157.1 ppm and the C-N at 147.0-148.0 ppm both lost a 6-7 Hz long range (3 bond C-C-C-H) carbon-hydrogen coupling when the hydrogen frequency 7.60-7.72 ppm had been irradiated. Hence, the long-range C-H interaction could *only* originate from C(O)-27 coupled with H-25,29 and C(N)-4 coupled with H-25,29. Decoupling of the other meta-ether hydrogen atoms H-19,23 would not affect any of the 2 C-N carbons. This experiment leads to the unequivocal assignment of H-20,22 and H-26,28 which are essential for the DS calculations. The assignment of H-25,29 and H-19,23 were also derived from this experiment. Further 1D and 2D heteronuclear (C and H) NMR experiments confirmed the previous assignments. Table 2 and 3 list the chemical shift of the ¹H and ¹³C-NMR spectra of PPEK respectively respectively.

The paragraph following Table 3 on page 10 is amended to read:

The hydrogen absorption at low field (8.54-8.68 ppm) is strongly believed to arise from H-16 (Figure 2) although it could not be formally proved. The chemical shift position of many peaks in ¹H and ¹³C-NMR spectra is seen to be not averaged out as would be the case where free rotation occurs. It is believed that PPEK is hindered by restricted rotation around certain linkages. In a “restricted” structure, H-16 would have an intensity of 1, as observed, and also would be in close proximity to the phthalazinone

carbonyl. The proximity to the carbonyl would deshield H-16 more than any other hydrogen atoms nearby one of the carbonyl groups of PPEK.

The paragraphs bridging pages 10 and 11 is amended to read:

A ^1H -NMR of PPEK in CD_2Cl_2 was acquired and the integration value of the up-field H-26,28 and H-20,22 absorptions was set to 4.00. The integration values of the other regions of the spectra corresponded exactly (table 2) to the number of hydrogen atoms expected from the chemical structure of PPEK repeat unit. Similarly, in a quantitative ^{13}C -NMR experiment, the upfield carbon signals C-26,28 and C-20,22 were also set to an intensity of 4.00 and the integration values of the other peaks again matched precisely. Sulfonated PPEK is only soluble in highly polar solvents and DMSO-d_6 was chosen to dissolve SPPEK. Spectra of SPPEK DS 1.03 and 1.63 are displayed in Figure 3 not shown. In comparison with PPEK, several new signals for the SPPEK derivatives appear with different chemical shifts due to the different solvents used and perturbation by different DSs of $-\text{SO}_3\text{H}$ groups. The ortho-ether hydrogen atoms remained at high field but their intensity decreased as they were replaced by $-\text{SO}_3\text{H}$ groups. More importantly, the ratio of low field H-16 (8.40-8.55) ppm to multiple peaks 7.60-8.40 ppm (which do not include ortho-ether protons) always remained 1.00:11.00 for low and high sulfonation degrees. This is proof that substitution occurred only at the ortho-ether sites of the PPEK repeat unit. Another phenomenon supporting this is the variation in size of the small high-field signal at 7.30-7.40 ppm due to mono-substitution on SPPEK repeat units. When strong electron withdrawing sulfonic acid groups are attached to benzene rings, they induce deshielding of hydrogen in the ortho and para positions. In monosubstituted SPPEK (DS~1), H-20 is deshielded by the $-\text{SO}_3\text{H}$ group hence shifted downfield.

In disubstituted SPEEK repeat units (DS>1), H-20 is still deshielded by the $-\text{SO}_3\text{H}$ group present on the phenol ring but it is also shielded by the proximity through space of the electron-rich oxygen atoms of the other $-\text{SO}_3\text{H}$ group nearby on the other phenol ring. The DS was simply measured by presetting the integration value of the low field hydrogen absorptions to 12H (7.50-8.60 ppm) and determining the intensity value of the upfield hydrogen signals. This value represents the number of hydrogen atoms that have not been converted into $-\text{SO}_3\text{H}$ groups and therefore subtracting it from 4H (unmodified PPEK) gives a direct DS value for SPPEK.

The paragraph following the heading "FT-IR," on page 12, is amended to read:

Fourier Transform Infrared (FT-IR) Spectroscopy was used to confirm the pendant SO_3H group on the polymer chain. Figure 5 4 shows the FT-IR spectra of parent PPEK and its sulfonated derivatives with DSs of 1.03 and 1.63 respectively. In comparing these spectra, one can see that in addition to the predictable absorptions at 3400 cm^{-1} due to the stretching of the hydroxyls of SO_3H groups, the SPPEK absorption bands at 1020 and 1081 cm^{-1} are characteristic of the aromatic SO_3H symmetric and asymmetric stretching vibrations respectively. These two characteristic peaks increase with higher DS. In addition, the reaction can be readily followed by the signal at 1500 cm^{-1} related to 1,4-aromatic ring substitution. Introduction of SO_3H onto the aromatic ring induces the formation of two new absorptions at 1471 and 1475 cm^{-1} , which at higher sulfonation degree, completely replace the absorption at 1500 cm^{-1} . The introduction of sulfonic acid groups in the modified polymer is thus confirmed.

In the paragraph following the heading “Proton conductivity,” on page 16, a space is inserted after “water” in the first line, and the paragraph is amended to read:

Prior to conductivity measurements, all membrane samples were soaked in water 1 or 2 days for hydration. The effect of the DS on the conductivity of SPPEK is shown in Figure 6, which shows that the conductivity of SPPEK at room temperature increases with DS and reaches 2×10^{-2} S/cm for SPPEK with DS of 1.2. This value is similar to Nafion 117, which shows conductivity of 3×10^{-2} S/cm. Figure 7 6 also shows the influence of temperature on the conductivity for DS 1.0 and 1.2 SPPEKs. As can be seen, the conductivities of these two SPPEKs increase with increasing temperature up to 95°C and reach 4×10^{-2} S/cm and 6×10^{-2} S/cm, respectively. Conductivity of SPPEK with DS of 1.0 drops sharply after that, which is probably caused by the dehydration of membrane. Compared with Nafion 117, the drop in conductivity at 80°C occurs at a higher temperature for SPPEK.

In the paragraph following the heading “Conductivity,” on page 17, a space is inserted after “water” in the first line, and the paragraph is amended to read:

Prior to conductivity measurements, all membrane samples were soaked in water 1 or 2 days for hydration. Figure 8 7 shows the influence of temperature on the conductivity for SPPES and SPPEK with DS 1.0. As can be seen, the conductivity of SPPEK increases with increasing temperature up to 95°C and reaches 2×10^{-2} S/cm, then drops sharply after that, which is probably caused by the dehydration of membrane. The conductivity of SPPES increases with increasing temperature up to 106°C and reaches 4×10^{-2} S/cm, then drops. Compared with Nafion 117, the drop in conductivity at 80°C occurs at a higher temperature for SPPEK.

The following paragraph is redundant on page 17 (it also appears, in essentially identical form, on page 16), and is deleted:

~~Prior to conductivity measurements, all membrane samples were soaked in water 1 or 2 days for hydration. The effect of the DS on the conductivity of SPPEK is shown in Figure 9, which shows that the conductivity of SPPEK at room temperature increases with DS and reaches 2×10^{-2} S/cm for SPPEK with DS of 1.2. This value is similar to Nafion 117, which shows conductivity of 3×10^{-2} S/cm. Figure 9 also shows the influence of temperature on the conductivity for DS 1.0 and 1.2 SPPEKs. As can be seen, the conductivities of these two SPPEKs increase with increasing temperature up to 95°C and reach 4×10^{-2} S/cm and 6×10^{-2} S/cm, respectively. Conductivity of SPPEK with DS of 1.0 drops sharply after that, which is probably caused by the dehydration of membrane. Compared with Nafion 117, the drop in conductivity at 80°C occurs at a higher temperature for SPPEK.~~